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MONITORING OF CATALYST PERFORMANCE IN CO_2 LASERS USING FREQUENCY MODULATION SPECTROSCOPY WITH DIODE LASERS

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Closed-cycle CO_2 laser operation with removal of O_2 and regeneration of CO_2 can be achieved by catalytic CO-O_2 recombination. Both parametric studies of the optimum catalyst formulation and long-term performance tests require on line monitoring of CO, O_2 and CO_2 concentrations.

There are several existing methods for molecular oxygen detection. These methods are either intrusive (such as electrochemical method or mass spectrometry[1]) or very expensive (such as CARS, UV laser absorption[2,3]).

We present here a high-sensitivity spectroscopic measurement of O_2 using two-tone frequency modulation spectroscopy (FMS) with a GaAlAs diode laser. Recently frequency modulation spectroscopy has been developed as a powerful method of doing highly sensitive, real-time spectroscopic measurements[4-8]. The theory of single-tone FMS and two-tone FMS have been studied and discussed in detail[4-6]. Since frequency modulation of diode lasers can be achieved by direct injection current modulation, FMS with near infrared diode lasers becomes a very attractive technique to make inexpensive, room-temperature spectroscopic probes for a variety of gases. It has been successfully used for water vapor absorption measurements at wavelengths near 815 nm[9] and methane absorption at wavelengths near 840 nm*. With careful selection, an inexpensive commercial laser diode can be obtained that is wavelength tunable from 760-770 nm, where the oxygen A band absorption occurs. This is the $v'=0 \leftarrow v''=0$ band of the magnetic dipole transition from the $X\,^3\Sigma_g^-$ ground electronic state to the excited $b\,^1\Sigma_g^+$ state. This band is known as the O_2 atmosphere band and has been well studied for line strengths, line widths and other spectroscopic parameters[10-13].

We have used a frequency modulation spectrometer, which was built at the University of Virginia, to make the O_2 spectroscopic measurement. Fig. 1 shows the schematic diagram of the frequency modulation spectrometer. A GaAlAs laser (Sharp LT030MF) operating at near 760 nm was mounted on a thermoelectrically cooled/heated block. The laser frequency is varied either by sweeping the injection current of the diode laser or by scanning its temperature with a tunability of 0.12 cm^{-1}/mA (3.6 GHz/mA) or 1.1 cm^{-1}/°C (33 GHz/°C), respectively. In the first case the injection current of the diode laser is swept by an internal function generator to provide straightforward injection-current tuning of the laser frequency. Injection-current tuning gives relatively fast scans (≈120 Hz) which permits us to monitor the FM signal directly on an

*L. G. Wang, unpublished data.

oscilloscope. This frequency modulation spectrometer also includes a computer-interfaced temperature controller to provide a slow scan of temperature and hence a slow scan of the frequency of the laser. The temperature controller provides a temperature stability of better than 0.01°C over several hours. A built-in automatic power controller stabilizes the laser output power within 2% when the laser temperature is varied from 10°C to 60°C. The GaAlAs diode laser is injection current modulated at two closely spaced frequencies (1 GHz ± 12 MHz) using capacitive coupling. The two-tone frequency modulated light from the laser is collimated by a 7-mm focal-length lens and passes through a 20-cm-long O_2 sample cell at approximately one atmosphere pressure. The 24 MHz rf beat signal of the two laser modulation frequencies is detected and amplified by using a photodetector (EG & G FND-100) and low-noise rf amplifiers. The signal is then phase detected by a mixer. Finally the signal is directed either through a 100-kHz low-pass filter to be displayed on an oscilloscope (i.e. for injection current tuning) or through a 0.8-Hz low-pass filter to be plotted on a plotter or to be stored into a computer (i.e. for temperature tuning).

Fig. 2 shows two-tone FMS signals of five Oxygen A band absorption lines. The absorption for these lines ranged from 0.8% to 1.2%. The O_2 A band consists of P and R branches. Due to the splitting of the ground electronic state rotational levels, each of these branches is composed of pairs of lines (PP and PQ for P branch; RR and RQ for R branch). The five absorption lines in Fig. 2 belong to the R branch of oxygen A band near 760 nm.

FMS* with diode lasers provides high detection sensitivity. Near quantum limit absorption sensitivity of 3×10^{-7} in a 0.8 Hz bandwidth for water vapor absorption lines has been reported[9]. A sensitivity of 10^{-6} can be easily obtained with a little care on eliminating the interference fringes. With a reference cell of O_2, the GaAlAs diode laser can be locked at a particular oxygen absorption line using an electronic feedback circuit. In this way the continuous monitoring of oxygen concentration in an on-line sample cell can be achieved. The minimum detectable (i.e. with S/N of 1) optical depth is estimated to be 5 ppm•meters with a 1-Hz bandwidth.

In conclusion, we have demonstrated a high-sensitivity spectroscopic measurement of O_2 using the two-tone FMS technique with a near infrared GaAlAs diode laser. Besides its inexpensive cost, fast response time, nonintrusive measurements and high sensitivity, this technique may also be used to differentiate between isotopes due to its high spectroscopic resolution.

This frequency modulation spectroscopy technique could also be applied for the on-line monitoring of CO and CO_2 using InGaAsP diode lasers operating in the 1.55 μm region and H_2O in the 1.3 μm region. The existence of single mode optical fibers at these near infrared region makes it possible to combine FMS with optical fiber technology. Optical fiber FMS is particularly suitable for making

*FMS is frequency modulation spectroscopy.

point-measurements at one or more locations in the CO_2 laser/catalyst system.

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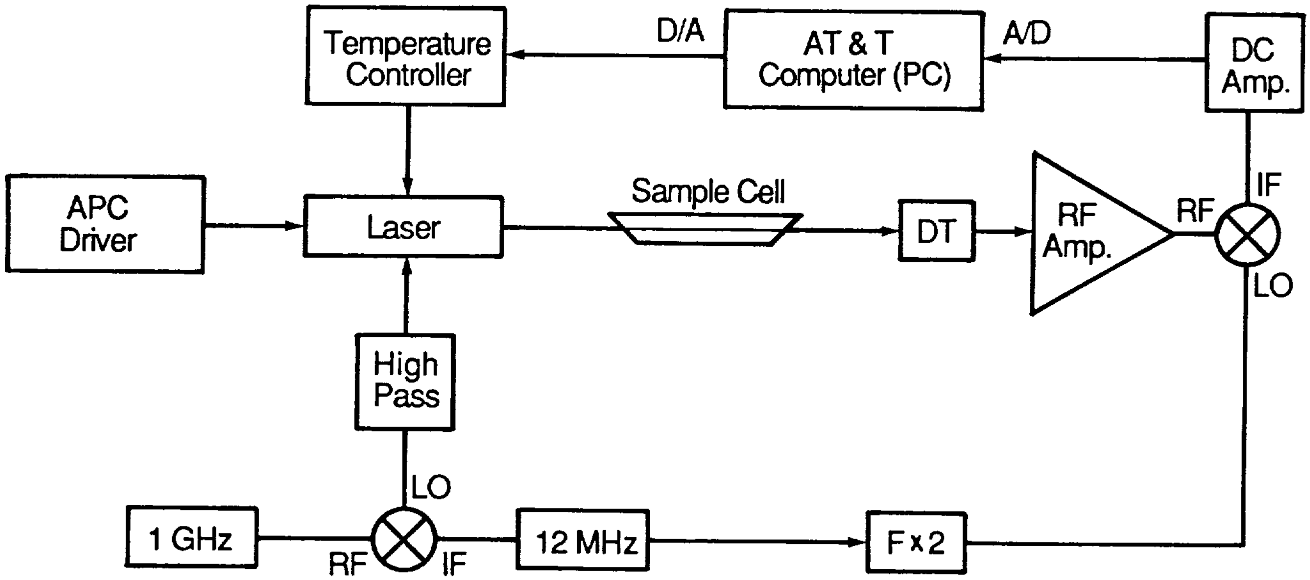

Figure 1. Experimental setup for two-tone frequency modulation spectroscopy.

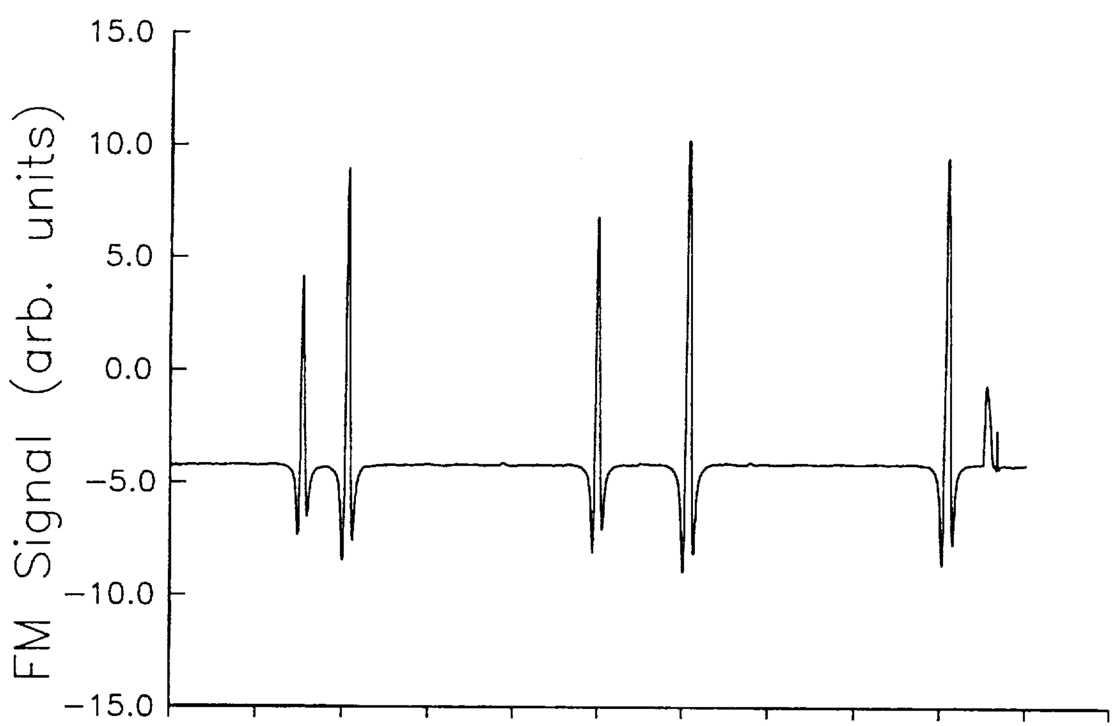

Figure 2. Two-tone FMS signal of five O_2 absorption lines.